

POLYMER CHEMISTRY

An Introduction

SECOND EDITION

Malcolm P. Stevens
University of Bath

New York Oxford
OXFORD UNIVERSITY PRESS
1990

2.5	Viscosity, 57
2.6	Molecular weight distribution, 59
2.6.1	Gel permeation chromatography (GPC), 61
2.6.2	Fractional solution, 63
2.6.3	Fractional precipitation, 65
2.6.4	Thin-layer chromatography (TLC), 65
2.6.5	Ultrafiltration, 66
	References, 66
	Review exercises, 67
3.	Chemical structure and polymer morphology, 70
3.1	Introduction, 70
3.2	Molecular weight and intermolecular forces, 71
3.3	The amorphous state—fictivity, 72
3.4	Glass transition temperature, 80
3.5	Stereochemistry, 85
3.6	Crystallinity, 91
3.7	Liquid crystallinity, 95
3.8	Chemical crosslinking, 98
3.9	Physical crosslinking, 99
3.10	Polymer blends, 100
	References, 104
	Review exercises, 107
4.	Chemical structure and polymer properties, 110
4.1	Introduction, 110
4.2	Fabrication methods, 110
4.3	Mechanical properties, 114
4.4	Thermal stability, 122
4.5	Thermal stability and flame resistance, 126
4.6	Chemical resistance, 128
4.7	Degradability, 131
4.8	Electrical conductivity, 134
4.9	Additives, 137
	References, 141
	Review exercises, 144
5.	Evaluation, characterization, and analysis of polymers, 146
5.1	Introduction, 146
5.2	Chemical methods of analysis, 147
5.3	Spectroscopic methods of analysis, 148
3.1.1	Infrared, 148
3.3.2	Raman, 149

5.3.3	Nuclear magnetic resonance, 151
5.3.4	Electron spin resonance, 156
5.3.5	Ultraviolet (UV)-visible, 157
5.3.6	Fluorescence, 157
5.4	X-ray, electron, and neutron scattering, 158
5.4.1	X-ray scattering, 158
5.4.2	Electron scattering, 159
5.4.3	Neutron scattering, 160
5.5	Characterization and analysis of polymer surfaces, 160
5.5.1	Scanning electron microscopy (SEM), 161
5.5.2	Attenuated total reflectance spectroscopy (ATR), 161
5.5.3	Photoacoustic spectroscopy (PAS), 162
5.5.4	Electron spectroscopy for chemical analysis (or applications) (ESCA) and Auger electron spectroscopy (AES), 163
5.5.5	Secondary-ion mass spectrometry (SIMS) and ion-scattering spectroscopy (ISS), 166
5.6	Thermal analysis, 167
5.6.1	Differential scanning calorimetry (DSC) and differential thermal analysis (DTA), 167
5.6.2	Thermochemical analysis (TMA), 168
5.6.3	Thermogravimetric analysis (TGA), 171
5.6.4	Pyrolysis-gas chromatography (PGC), 171
5.6.5	Flammability testing, 173
5.7	Measurement of mechanical properties, 176
5.8	Evaluation of chemical resistance, 178
5.9	Evaluation of electrical properties, 178
	References, 180
	Review exercises, 183
PART II	VINYL POLYMERS
6.	Free radical vinyl polymerization, 189
6.1	Introduction, 189
6.2	Free radical initiators, 191
6.2.1	Peroxides and hydroperoxides, 191
6.2.2	Azo compounds, 194
6.2.3	Redox initiators, 194
6.2.4	Photoinitiators, 195
6.2.5	Thermal polymerization, 195
6.3	Techniques of free radical polymerization, 196
6.3.1	Bulk, 196
6.3.2	Suspension, 197

- 6.3.3. *Solution*, 197
 6.3.4. *Emulsion*, 198
 6.4. Kinetics and mechanism of polymerization, 199
 6.5. Stereochemistry of polymerization, 209
 6.6. Polymerization of dienes, 212
 6.6.1. *Isolated dienes*, 212
 6.6.2. *Conjugated dienes*, 213
 6.7. Monomer reactivity, 216
 6.8. Copolymerization, 221
 References, 229
 Review exercises, 231
7. Vinyl polymerization with ionic and group transfer initiators, 234
 7.1. Introduction, 234
 7.2. Cationic polymerization, 235
 7.2.1. *Cationic initiators*, 235
 7.2.2. *Mechanism, kinetics, and reactivity in cationic polymerization*, 237
 7.2.3. *Stereochemistry of cationic polymerization*, 244
 7.2.4. *Cationic copolymerization*, 247
 7.2.5. *Isomerization in cationic polymerization*, 249
 7.3. Anionic polymerization, 250
 7.3.1. *Anionic initiators*, 250
 7.3.2. *Mechanism, kinetics, and reactivity in anionic polymerization*, 252
 7.3.3. *Stereochemistry of anionic polymerization*, 256
 7.3.4. *Anionic copolymerization*, 259
 7.4. Group transfer polymerization, 262
 References, 266
 Review exercises, 268
8. Vinyl polymerization with complex coordination catalysts, 271
 8.1. Introduction, 271
 8.2. Ziegler-Natta catalysts, 273
 8.3. Mechanism and reactivity in Ziegler-Natta polymerization, 276
 8.4. Stereochemistry of Ziegler-Natta polymerization, 281
 8.5. Polymerization of dienes with Ziegler-Natta catalysts, 283
 8.6. Metathesis polymerization, 285
 8.7. Ziegler-Natta copolymerization, 289
 8.8. Supported metal oxide catalysts, 291
 8.9. Affin catalysts, 292
 References, 293
 Review exercises, 294
9. Reactions of vinyl polymers, 296
 9.1. Introduction, 296
 9.2. Functional group reactions, 297
 9.2.1. *Introduction of new functional groups*, 297
 9.2.2. *Conversion of functional groups*, 299
 9.3. Ring-forming reactions, 301
 9.4. Crosslinking, 303
 9.4.1. *Vulcanization*, 303
 9.4.2. *Radation crosslinking*, 305
 9.4.3. *Photochemical crosslinking*, 306
 9.4.4. *Crosslinking through labile functional groups*, 310
 9.4.5. *Ionic crosslinking*, 311
 9.5. Block and graft copolymer formation, 312
 9.5.1. *Block copolymers*, 312
 9.5.2. *Graft copolymers*, 313
 9.6. Polymer degradation, 317
 9.6.1. *Chemical degradation*, 317
 9.6.2. *Thermal degradation*, 318
 9.6.3. *Degradation by radiation*, 320
 References, 321
 Review exercises, 323
- PART III. NONVINYL POLYMERS
10. Step-reaction and ring-opening polymerization, 329
 10.1. Introduction, 329
 10.2. Step-reaction polymerization—kinetics, 329
 10.3. Stoichiometric imbalance, 335
 10.4. Molecular weight distribution, 337
 10.5. Network step polymerization, 339
 10.6. Step-reaction copolymerization, 342
 10.7. Step polymerization techniques, 343
 10.8. Ring-opening polymerization, 346
 References, 349
 Review exercises, 350
11. Polyethers, polysulfides, and related polymers, 352
 11.1. Introduction, 352
 11.2. Preparation of polyethers by chain-reaction and ring-opening polymerization, 352
 11.2.1. *Polymerization of carbonyl compounds*, 352
 11.2.2. *Stereochemistry of dialdehyde polymerization*, 358



11 12



Apart from some limited applications with styrene, thermal polymerization has been used commercially only with certain polymers or oligomers end-capped with thermally labile moieties such as maleimide or malimide for manufacture of composites (see Chapter 4, Table 4.4).

6.3 Techniques of free radical polymerization

Free radical polymerization can be accomplished in bulk, suspension, solution, or emulsion. Each of these methods has advantages and disadvantages, as outlined in Table 6.2. In addition, work has also been done on solid- and gas-phase polymerizations of vinyl monomers, but these are of lesser importance. Because polymers are not volatile, the term *gas-phase polymerization* means, in effect, bulk polymerization in which monomer vapors diffuse to the polymerization site. A special case of solid-phase polymerization involving inclusion complexes is discussed in Section 6.6.

6.3.1 Bulk

Bulk polymerization is simplest, from the standpoint of termination and equipment, but it is also the most difficult to control, particularly when the polymerization reaction is very exothermic. This, coupled with problems of heat transfer as the monomer-polymer solution increases in viscosity, limits the use of bulk methods in commercial production, although more efficient bulk processes have been developed in recent years.

In cases where polymer is insoluble in monomer, polymer precipitates and the viscosity of the medium does not change appreciably. Problems will arise, however, as a result of free radicals being detectable by ESR being involved in the polymer droplet, which can lead to *autoacceleration*, that is, a rapid increase in the polymerization rate.¹ In some instances, particularly with diene monomers, this acceleration effect may lead to formation of insoluble crosslinked polymer nodules, a phenomenon referred to as *polymer gelation*.² The crosslinked nodules are usually of light weight and occupy considerably more volume than the monomers from which they are derived, which may cause swelling and even fracture of the polymerization apparatus.

Table 6.2. Free radical polymerization techniques

Method	Advantages	Disadvantages
Bulk	Simple, no contaminants added	Reaction exotherm difficult to control, high viscosity
Suspension	Heat readily dispersed; low viscosity; polymer obtained in granular form and may be used directly	Reaction exotherm difficult to control, agglomeration may occur, contamination by stabilizer
Solution	Heat readily dispersed; low viscosity; may be used directly as solution	Added cost of solvent; solvent difficult to separate; possible chain transfer with solvent; possible environmental pollution
Emulsion	Heat readily dispersed; low viscosity; high molecular weight obtained; works on lumpy polymers	Contamination by stabilizer and other emulsion components; reaction often needs to be controlled by swelling and drying necessary for bulk polymer

The major commercial uses of bulk vinyl polymerization are in casting formulations and low-molecular-weight polymers for use as adhesives, plasticizers, tackifiers, and lubricant additives.

6.3.2 Suspension

Suspension polymerization involves mechanically dispersing monomer in a noncompatible liquid, usually water, and polymerizing the resultant monomer droplets by use of a monomer-soluble initiator. Monomer is kept in suspension by continuous agitation and the use of *stabilizers* such as poly(vinyl alcohol) or methyl cellulose. If the process is carefully controlled, polymer is obtained in the form of granular beads, which are easy to handle and can be isolated by filtration or by sparging into a thermal chamber (*spay drying*). A major advantage is that heat transfer is very efficient and the reaction is therefore easily controlled. Suspension polymerization cannot be used for tacky polymers such as elastomers because of the tendency for agglomeration of polymer particles. From the standpoint of kinetics and mechanism, suspension polymerization is identical to bulk polymerization. Suspension methods are used to prepare a number of granular polymers, including polystyrene, poly(vinyl chloride), and poly(methyl methacrylate).

6.3.3 Solution

Like suspension, solution polymerization allows efficient heat transfer. Solvent must be chosen carefully, otherwise chain transfer reactions discussed in

the next section) may severely limit the molecular weight. Because of problems in removing solvent completely from the resultant polymer, the method is best suited to applications where the solution may be used directly, as with certain adhesives or solvent-based paints.

6.3.4 Emulsion

Developed at Goodyear Tire and Rubber Company in the 1920s, emulsion polymerization resembles suspension polymerization in that water is used as a dispersing medium and heat transfer is very efficient, but there the similarity ends. In 1% monomer is dispersed in the aqueous phase by an emulsifying agent such as a soap or detergent. Initiator radicals, usually of the redox type, are generated in the aqueous phase and diffuse into soap micelles swollen with monomer molecules. As monomer is used up in the polymerization reaction, more monomer migrates into the micelles, and thus the reaction continues. Termination of polymerization occurs by radical combination when a new radical diffuses into the micelle. Because only one radical is present in the micelle prior to termination, extremely high molecular weights are obtainable, generally too high to be of practical value unless compounds called *chain transfer agents* are added that control the degree of polymerization. (How chain transfer agents work is discussed later in the chapter.) The

overall process is complex, with reaction kinetics differing significantly from that of bulk or solution processes.

Emulsion polymerization is widely used in industry for large-scale preparations, and is particularly useful for manufacturing water-based (latex) paints or adhesives in which the emulsified product is used directly. Emulsion polymerization is also suitable for preparing tacky polymers because the very small particles are stable and resist agglomeration. Two typical emulsion recipes are given in Table 6.3.

A much less commonly used emulsion technique involves dispersing an aqueous solution of monomer in a nonaqueous phase. This is referred to as an *inverse or water-in-oil* emulsion (as opposed to the more conventional *oil-in-water* type). The mechanism of polymerization is similar for the two techniques, but inverse emulsions tend to be less stable.

6.4 Kinetics and mechanism of polymerization

Initiation of free radical chain polymerization involves two reactions: formation of the initiator radical (6.22), and addition of the initiator radical to monomer (6.23). Evidence for the incorporation of initiator radicals arises from spectroscopic and chemical analysis of end groups. Addition of monomer radical to another monomer molecule, followed by successive additions of oligomer and polymer radicals to available monomer (6.24), comprise the propagation reactions.



It was mentioned in Chapter 3 (Section 3.5) that each addition step follows the predominant *head-to-tail* orientation shown in reaction (6.24). This is due to a combination of steric and electronic effects. Steric repulsion favors attack by the radical at the least hindered carbon of the double bond, and resonance stabilization favors formation of the more stable free radical. Head-to-tail polymerization does not occur exclusively. Significant amounts of *head-to-head* structures have been found (by ¹⁹F-NMR spectroscopy) to occur in certain fluorine-containing polymers,¹⁸ notably poly(vinyl fluoride) (13) and

Table 6.3. Typical emulsion polymerization recipes^a

Ingredients, conditions	Styrene-butadiene copolymer	Polyacrylate latex
Ingredients (parts by weight)		
Water	190	133
Butadiene	70	—
Styrene	30	—
Ethyl acrylate	—	93
2-Chloroethyl vinyl ether	—	5
p-Dioxybenzene	—	2
Soap	5	3 ^b
Potassium persulfate	0.3	1
n-Dodecyl mercaptan	0.5	—
Sodium pyrophosphate	—	0.7
Conditions		
Time	12 hr	8 hr
Temperature	50°C	60°C
Yield	65%	~100%

^aRecipes from Cooper.¹⁹

^bSodium lauryl sulfate.